Adsorption of Halides at the Mercury-Water Interface

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## Introduction

Recent discussions (2, 3, 4) of the measurement of adsorption of ions at the mercury-water interface have suggested that discrepancies exist between the two principal methods of obtaining these results: electrocapillary measurements and capacity measurements. It has been suggested that some of the discrepancies are due to inevitable inaccuracies in the computation of data by the different routes and that some arise from essential differences in the quantities measured.

In order to assess the situation, existing capacity data on KCl (5) and KI (6), together with new data on KBr, are compared with electrocapillary data (7, 8, 9, 10) with particular attention to the accuracy with which the required data can be obtained.

## Experimental

Measurements of the double layer capacity of mercury in aqueous KBr solution were made using the bridge previously described (11). The balance point was usually taken just after the eighth second on a drop whose total life was 10 - 12 seconds, but the capacity was checked over the range between the 4th and 10th second to ensure independence of the drop age. Similar checks were made in the frequency range from 600 c/s to 3 kc/s. No frequency dependence was observed and measurements were made at 1 kc/s. Reproducibility of capacities within a given run was 0.05% while that from one run to another was 0.15%. The flow rate of Hg (normally about 0.2 mg s$^{-1}$) was determined by collecting mercury over an accurately timed (1 kc/s tuning fork + dekatron scaler) interval, drying and weighing. It remained constant within 0.2%. Thin-walled, tapering capillaries were drawn from 1 mm bore capillary tubing, selected by trial and siliconed by brief exposure to dichloro-dimethyl silane vapor followed by wet nitrogen. The tip was then recut to ensure that the solution should wet the horizontal surface of the tip. The potential of the electrocapillary maximum was determined by the streaming electrode method (12) and was reproducible to 0.5 mV. All potentials were measured using a Croydon type P3 potentiometer and a Pye "Scalamp" 1400 $\Omega$ galvanometer. The reference electrode was a 0.1 M KCl calomel electrode joined to a reservoir containing 0.1 M KBr. This solution was then put in contact with the working solution of KBr, forming the junction in a tap. Both these liquid junctions were stable and potentials were reproducible to 0.1 mV. All measurements were made with the cell immersed in a water thermostat at 25°C. Mercury was purified by a wet process followed by three distillations in a Hulett still (13). Laboratory distilled water was redistilled from dilute alkaline permanganate in a still with special splash traps. BDH Analar KBr was dissolved in this water.

## Results and Analysis

Measurements were made of the capacity and potential of the electro-

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capillary maximum at ten concentrations of KBr from 0.005 M to 5 M. The interfacial tension at the electrocapillary maximum was obtained by plotting the experimental values found by Gouy (7) and by Devanathan and Peries (9) as a function of log activity and interpolating. Small differences exist between the two sets of electrocapillary data but it is unlikely that errors exceed 0.2 dyn cm$^{-1}$ at concentrations below 1 M; at higher concentrations they may rise to 0.5 dyn cm$^{-1}$. The capacity-potential curves were integrated with the aid of a computer (Elliott 503) using a program written in Algol but similar to that described previously (14) in the first routine where values of the function $\xi_{\pm} = \gamma + q E_{\pm}$ are calculated. Here $\gamma$ is the interfacial tension, q the charge on the metal and $E_{\pm}$ the potential of the mercury electrode with respect to an electrode reversible to the cation (+ subscripts) or anion (- subscripts). The new program further fits the pairs of values of $\xi_{\pm}$ and log activity at a given value of q to a power series by the method of least squares. The ionic surface excesses are then calculated according to the appropriate form of the electrocapillary equation (15)

$$(\partial \xi_{\pm}/RT \partial \ln a_{\pm}^2 )_q \;\; = \;\; -\Gamma_{\mp} \;\; = \;\; -q_{\mp} / z_{\mp} e$$

From the charge due to the cation, the program then uses Gouy-Chapman theory ( to calculate outer Helmholtz potential ($\phi_2$) and the charge in the diffuse layer due to the anion. Finally, the charge ($q_-^i$)due to specifically adsorbed anions and the potential drop ($\phi^{M-2}$) across the inner layer are computed. Some typical results are shown in Tables 1, 2, and 3.

## Discussion

Direct comparison of the integrated capacity curves with the electro-capillary curves measured by Devanathan and Peries (9) is possible at 0.01, 0.1, and 1 M. Deviations between the two curves are never greater than 1 dyn cm$^{-1}$ in the range +24 to -18 $\mu$Ccm$^{-2}$ and more often of the order of 0.1 dyn cm$^{-1}$. Thus in this system there appears to be little doubt that the two methods of measurement are in agreement within experimental error. Similar conclusions may be drawn from a comparison of the integral of Grahame's data (5, 6) for 0.1 M and 1 M KCl, 0.015 M, 0.1 M and 1 M KI with electrocapillary results (7, 8, 9, 10). The integral of Grahame's capacity data for 0.1 M NaF agrees well with electrocapillary data on 0.1 M NH$_4$F obtained in Bristol by Dr. E. Dutkiewicz; small divergencies occur

on the anodic branch amounting to 1.6 dyn cm$^{-1}$ at +10 $\mu$C cm$^{-2}$. Agreement in dilute solutions of weakly adsorbed electrolytes is poorer, as already mentioned (14, 4) with H$_2$PO$_4^-$ and Cl$^-$. The appearance of the diffuse layer minimum in the capacity curve is an indication of conditions under which such disagreement may be expected. In the case of H$_2$PO$_4^-$, where the dis-agreement is large, evidence was presented (14) supporting the proposal that the electrocapillary data is in error under these conditions.

Comparison of charge-potential curves derived from the two types of measurement confirms that they are usually in good agreement within the errors to be expected from graphical differentiation of electrocapillary curves. This accuracy will depend on the spacing of experimental points; 50 mV inter-vals have been usual in recent studies (9, 14, 17). Comparison of the present results with those of Devanathan and Peries (9) suggests that the general trend is in good agreement though a scatter of 1 $\mu$C cm$^{-2}$ in individual points is fairly frequent. At the far anodic end when the charge is greater than 20 $\mu$C cm$^{-2}$ and both the electrocapillary curve and the capacity curve are very steep, the errors may be much larger. Electrocapillary curves were also differentiated using a computer following a procedure based on an unpublished suggestion by D. C. Grahame. From the set of $\gamma$-E points a new set of points y-E was computed where y = $\gamma$ + q*E, q* being a constant. The curve y-E now has a maximum at the value of E for which q* is the slope of the original $\gamma$-E curve. Thus, by repeating this procedure a set of values of E corresponding to given values of q* may be found. The value of y at the maximum of the y-E curve is, of course,

the value of $\xi$ corresponding to $q^*$ and the fact that the y-E curve has a flat maximum shows that $\xi$ may be obtained with accuracy comparable to the original values of $\gamma$. In fact, the calculation of $\xi$ does not depend upon an accurate differentiation of the electrocapillary curve in contrast to the remark of Devanathan and Tilak (3). This procedure is thus excellent for converting from $\gamma$ to $\xi$ but does not produce charge-potential curves of any greater accuracy than those from graphical differentiation.

Direct comparison of twice differentiated electrocapillary curves with capacity curves again confirms qualitatively the agreement between the two types of measurement, but the inaccuracies introduced by differentiation are too great to allow more quantitative conclusions.

The most important information obtained from capacity and electro-capillary measurements concerns the ionic composition of the double layer. This is obtained by the application of Gibbs adsorption equation in one form or another and necessarily involves a differentiation step, although this may be carried out by fitting integrated theoretical isotherms to the experimental data (15) and then differentiating analytically. Such a procedure has particular advantages if the isotherm constants are independent of charge, but there is a risk of imposing this condition on a set of data since the surface-pressure curve is not very sensitive to variations in isotherm constants. A more direct procedure might therefore have advantages. The computer program described above is an attempt to solve this problem in a simple way. In fitting a polynomial to the $\xi_\pm$ - $\ln a_\pm$ points different degrees of polynomial were examined. High-order polynomials produce results that are too sensitive to experimental error and are consequently meaningless. The criterion adopted was that of comparing the results of an n-th order fits with that of an (n + 1) th order fit. Best agreement was obtained when n = 3. Even so, the end points produced large variations, the results being less plausible for the 4th than for the 3rd order fit. It is, therefore, recommended that a 3rd order polynomial provides the most satis-factory simple route to the differentiation of $\xi_\pm$ — $\ln a_\pm$ curves. Agreement with graphical differentiation for the KBr system was found to be within 0.3 $\mu C$ cm$^{-2}$ except at extreme concentrations or charges. The curves of $q^1$ against q can be compared directly with the results of Grahame and Söderberg (18) at 0.1 M and of Devanathan and Peries (9) at 0.01 M, 0.1 M, and 1 M. With the former no deviation is greater than 0.7 $\mu C$ cm$^{-2}$ while with the latter dis-crepancies of greater than 1 $\mu C$ cm$^{-2}$ are found undoubtedly as a result of errors introduced by graphical differentiation to obtain both $q^1$ and q.

As a further check the data of Grahame (6) for aqueous KI was put through the computer program using integration constants based on electrocap-illary data (7, 8, 9, 10). In this case the agreement between the 3rd and 4th order fits was much better and at the lower concentrations good agreement with the published data (6) was obtained. The results obtained from this system are undoubtedly better primarily because the concentration points are more closely spaced. Grahame (6) measured capacities at 17 concentrations between 0.015 M and 1.2 M; that is, over 8 points per decade. The present KBr results are based on 3 points per decade and must be correspondingly less accurate. This must be considered as the main weakness of much recent work on the electrical double layer (14, 19) especially that based on 2 points per decade (9, 17).

At concentrations of the order of 1 M and higher the computed KI results differ from the published data (6) owing to the effect of the thickness of the inner layer previously discussed (5). In spite of contrary assertions (2) there seems good reason to suppose that the correction for this effect is charge dependent (14). Since no way of measuring this effect in the presence of specific adsorption has been devised, values of $q^1$ for solutions of higher con-centrations are subject to error from this cause as well as from defects in diffuse layer theory.

Data from the dilute solutions calculated from capacity measurements with the aid of electrocapillary integration constants also appear to deviate by a micro-coulomb or two from the expected values at negative charge, as

commented upon recently (19). It is possible that this may be the result of the slow transport of ions to the double layer (20, 21) but a clear proof that this is the cause is at present lacking.

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Table 1                        0. 01 M KBr in water at 25°C

| $q$ $\mu C\ cm^{-2}$ | $-E$ V | $C$ $\mu F\ cm^{-2}$ | $q_+$ $\mu C\ cm^{-2}$ | $q_-^1$ $\mu C\ cm^{-2}$ | $\phi_2$ mV | $\phi^{M-2}$ mV | $\gamma$ $dyn\ cm^{-1}$ |
|---|---|---|---|---|---|---|---|
| -18 | 1. 592 | 17. 59 | 16. 0 | 1. 4 | -172 | -958 | 329. 8 |
| -16 | 1. 475 | 16. 65 | 14. 0 | 1. 5 | -165 | -848 | 349. 7 |
| -14 | 1. 353 | 16. 04 | 12. 1 | 1. 4 | -158 | -733 | 368. 0 |
| -12 | 1. 227 | 15. 90 | 10. 2 | 1. 3 | -150 | -616 | 384. 3 |
| -10 | 1. 102 | 16. 16 | 8. 3 | 1. 1 | -140 | -500 | 398. 1 |
| - 8 | 0. 982 | 17. 04 | 6. 5 | 1. 0 | -128 | -392 | 408. 9 |
| - 6 | 0. 868 | 18. 24 | 4. 5 | 1. 0 | -111 | -295 | 416. 9 |
| - 4 | 0. 761 | 18. 88 | 2. 5 | 1. 0 | - 86 | -213 | 422. 3 |
| - 2 | 0. 656 | 19. 76 | + 0. 8 | + 0. 8 | - 46 | -149 | 425. 4 |
| 0 | 0. 572 | 29. 08 | 0. 0 | 0. 0 | 0 | -105 | 426. 3 |
| + 2 | 0. 512 | 37. 75 | - 0. 1 | - 1. 8 | + 8 | - 58 | 425. 7 |
| 4 | 0. 463 | 42. 74 | + 0. 1 | - 4. 1 | - 5 | + 4 | 424. 3 |
| 6 | 0. 417 | 43. 75 | 0. 3 | - 6. 6 | - 23 | 69 | 422. 0 |
| 8 | 0. 371 | 45. 09 | 0. 7 | - 9. 0 | - 41 | 131 | 418. 8 |
| 10 | 0. 328 | 46. 40 | 1. 2 | -11. 5 | - 56 | 190 | 414. 9 |
| 12 | 0. 286 | 51. 51 | 1. 7 | -14. 1 | - 69 | 245 | 410. 32 |
| 14 | 0. 250 | 60. 00 | 2. 2 | -16. 7 | - 81 | 293 | 405. 6 |
| 16 | 0. 220 | 72. 20 | 2. 9 | -19. 4 | - 92 | 334 | 401. 1 |
| 18 | 0. 191 | 95. 88 | 3. 5 | -22. 0 | -100 | 371 | 396. 3 |
| 20 | 0. 173 | 130. 9 | 4. 0 | -24. 5 | -106 | 395 | 392. 9 |
| 22 | 0. 160 | 165. 1 | 4. 6 | -27. 2 | -112 | 415 | 390. 0 |
| 24 | 0. 144 | 231. 0 | 5. 2 | -29. 7 | -118 | 436 | 386. 7 |

# Table 2

**1 M KBr in water at 25 C**

| $q$ | $-E$ | $C$ | $q_+$ | $q_-^1$ | $\phi_2$ | $\phi^{M-2}$ | $\gamma$ |
|---|---|---|---|---|---|---|---|
| $\mu C\,cm^{-2}$ | V | $\mu F\,cm^{-2}$ | $\mu C\,cm^{-2}$ | $\mu C\,cm^{-2}$ | mV | mV | $dyn\,cm^{-1}$ |
| -18 | 1.488 | 18.09 | 13.0 | 0.9 | -60 | -969 | 334.0 |
| -16 | 1.373 | 17.09 | 11.3 | 0.9 | -55 | -859 | 353.4 |
| -14 | 1.254 | 16.71 | 9.7 | 0.6 | -50 | -746 | 371.2 |
| -12 | 1.136 | 17.13 | 8.4 | 0.2 | -46 | -632 | 386.7 |
| -10 | 1.025 | 19.28 | 7.4 | - 0.7 | -42 | -524 | 398.9 |
| - 8 | 0.931 | 24.10 | 7.0 | - 2.2 | -40 | -432 | 407.4 |
| - 6 | 0.858 | 30.94 | 7.1 | - 4.3 | -41 | -359 | 412.5 |
| - 4 | 0.799 | 37.50 | 7.6 | - 6.9 | -43 | -298 | 415.45 |
| - 2 | 0.750 | 43.16 | 8.4 | - 9.8 | -46 | -246 | 417.0 |
| 0 | 0.705 | 45.87 | 9.3 | -12.8 | -49 | -198 | 417.4 |
| + 2 | 0.663 | 48.05 | 10.1 | -15.8 | -52 | -153 | 417.0 |
| + 4 | 0.621 | 48.80 | 10.9 | -18.7 | -54 | -109 | 415.7 |
| + 6 | 0.581 | 49.56 | 11.7 | -21.6 | -56 | - 66 | 413.7 |
| + 8 | 0.540 | 48.48 | 12.5 | -24.5 | -59 | - 23 | 410.9 |
| +10 | 0.499 | 49.63 | 13.3 | -27.4 | -61 | + 20 | 407.2 |
| +12 | 0.460 | 53.67 | 14.1 | -30.2 | -63 | 61 | 402.9 |
| +14 | 0.425 | 60.42 | 14.9 | -33.1 | -65 | 98 | 398.3 |
| 16 | 0.394 | 69.34 | 15.6 | -35.8 | -67 | 131 | 393.6 |
| 18 | 0.367 | 80.57 | 16.3 | -38.6 | -68 | 160 | 389.1 |
| 20 | 0.343 | 94.77 | 17.0 | -41.4 | -70 | 186 | 384.5 |
| 22 | 0.323 | 113.1 | 17.7 | -44.1 | -71 | 206 | 380.5 |
| 24 | 0.307 | 132.2 | 18.3 | -46.7 | -73 | 224 | 376.7 |

# Table 3

**0.1 M KBr in water at 25 C**

| $q$ | $-E$ | $C$ | $q_+$ | $q_-^1$ | $\phi_2$ | $\phi^{M-2}$ | $\gamma$ |
|---|---|---|---|---|---|---|---|
| $\mu C\,cm^{-2}$ | V | $\mu F\,cm^{-2}$ | $\mu C\,cm^{-2}$ | $\mu C\,cm^{-2}$ | mV | mV | $dyn\,cm^{-1}$ |
| -18 | 1.543 | 17.79 | 17.6 | - 1.3 | -121 | -962 | 331.7 |
| -16 | 1.428 | 16.87 | 15.5 | - 1.1 | -115 | -853 | 351.4 |
| -14 | 1.307 | 16.24 | 13.3 | - 0.9 | -108 | -739 | 369.5 |
| -12 | 1.182 | 16.03 | 11.0 | - 0.6 | -100 | -623 | 385.6 |
| -10 | 1.059 | 16.40 | 8.9 | - 0.4 | - 90 | -508 | 399.3 |
| - 8 | 0.940 | 17.57 | 6.9 | - 0.3 | - 80 | -400 | 409.9 |
| - 6 | 0.833 | 20.17 | 5.3 | - 0.7 | - 69 | -304 | 417.4 |
| - 4 | 0.745 | 25.87 | 4.2 | - 1.5 | - 61 | -223 | 421.9 |
| - 2 | 0.678 | 33.90 | 3.8 | - 3.0 | - 57 | -160 | 424.0 |
| 0 | 0.624 | 41.56 | 3.8 | - 5.1 | - 58 | -107 | 424.5 |
| + 2 | 0.578 | 45.58 | 4.1 | - 7.4 | - 60 | - 59 | 424.1 |
| + 4 | 0.536 | 47.56 | 4.5 | - 9.8 | - 63 | - 13 | 422.8 |
| + 6 | 0.494 | 47.87 | 4.9 | -12.2 | - 66 | + 33 | 420.7 |
| + 8 | 0.452 | 48.20 | 5.4 | -14.8 | - 70 | 78 | 417.8 |
| +10 | 0.411 | 50.29 | 5.9 | -17.3 | - 74 | 122 | 414.1 |
| +12 | 0.373 | 56.50 | 6.5 | -14.9 | - 77 | 164 | 404.9 |
| 14 | 0.341 | 65.56 | 7.0 | -22.5 | - 81 | 200 | 405.7 |
| 16 | 0.312 | 73.86 | 7.6 | -25.1 | - 84 | 232 | 401.4 |
| 18 | 0.285 | 87.43 | 8.2 | -27.7 | - 87 | 262 | 396.9 |
| 20 | 0.265 | 105.7 | 8.8 | -30.3 | - 90 | 285 | 392.9 |
| 22 | 0.242 | 144.4 | 9.3 | -32.9 | - 92 | 310 | 388.5 |
| 24 | 0.230 | 189.5 | 9.8 | -35.4 | - 95 | 324 | 385.7 |